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## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

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<b>(21) International Application Number:</b> PCT/EP94/00107 <b>(22) International Filing Date:</b> 17 January 1994 (17.01.94)  <b>(30) Priority Data:</b> 104.441 19 January 1993 (19.01.93) IL  <b>(71) Applicants (for all designated States except US):</b> RAPAPORT, Erich [AT/IL]; 87 University Street, 69345 Tel Aviv (IL). YISSUM RESEARCH DEVELOPMENT COMPANY OF THE HEBREW [IL/IL]; UNIVERSITY OF JERUSALEM, 46 Jabotinsky Street, 91042 Jerusalem (IL).  <b>(72) Inventor; and</b> <b>(75) Inventor/Applicant (for US only):</b> NUSSINOVITCH, Amos [IL/IL]; 48 Ein Ganim Street, 49444 Petach-Tikva (IL).  <b>(74) Agent:</b> KRAUS, Walter; Kraus, Weisert & Partner, Thomas-Wimmer-Ring 15, D-80539 Munich (DE).		<b>(81) Designated States:</b> AU, CA, US, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).  <b>Published</b> <i>With international search report.</i>
<b>(54) Title:</b> SPONGES OF HYDROCOLLOIDS  <b>(57) Abstract</b>  The invention provides sponges (foams) produced from hydrocolloids by the expansion of gels of these. The foams have properties which can be varied, such as water absorption, biodegradability, pore size and structure. Edible products can be produced which may contain an edible plasticizer, a sugar or sugar substitute and possibly also a flavoring agent or taste enhancer. The novel sponges are produced by preparing a gel of a hydrocolloid, and either sealing it in a closed vessel with a liquid of similar composition, pressurizing the vessel and abruptly releasing the pressure, followed by freeze drying, or by incorporating in such a gel a suitable microorganism, such as a yeast and inducing fermentation in the presence of a suitable nutrient medium, so that the carbon dioxide formed results in the expansion and foam formation, which is processed to the final product.		

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DESCRIPTION

## SPONGES OF HYDROCOLLOIDS

FIELD OF THE INVENTION

The invention relates to novel sponges which have a variety of textures, structures, water absorbing properties and biodegradability. Certain sponges of the invention can be used as edibles, and there can be produced low- high and  
5 ultra-high-calory content sponges. The latter are of special value where highly concentrated edibles are required. Certain types of sponges can be used in medicine and also in a variety of industries. Sponges according to the invention can be used in diapers, hygienic pads packaging material and  
10 the like.

BACKGROUND OF THE INVENTION

There is known a wide variety of spongy organic and inorganic materials. There are known open-cell sponges and closed cell ones. According to the present invention there can  
15 be provided edible sponges and sponges for a variety of uses, with controlled properties.

DESCRIPTION OF THE INVENTION

According to the invention the starting material for the production of sponges is one or more hydrocolloid, and there

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are produced air- or gas-filled structures of controlled parameters. It is an object of the invention to provide the food industry with a new carrier (matrix), which can be eaten nearly as is as a low calorie food, or filled with fat or  
5 other high calorie constituents via infusion or other processes. Only a few modifications at the factory level, are therefore required for production of two totally different product types.

Specially designed sponges are produced for use in the  
10 diaper and hygienic pad industries. The sponges can be compressed to a smaller volume, while maintaining their absorbing capacity, and return to a larger volume only upon absorbing liquids. The big advantage of these sponges is their biodegradability. Decomposition is complete after  
15 a few months, generally about six months, thereby eliminating the problem posed by the currently used raw materials.

Biological sponges, such as those described here can also be used as filling materials in biochemistry, as well as carriers of enzymes and related substances.

## 20 Sponge production: Materials and Examples

By air inclusion: Gels consisting of one hydrocolloid such as agar, carrageenan, gelatin, alginate, starch, pectin, gellan, kunjak mannan, two hydrocolloids, such as xanthan gum

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plus locust bean, or three or more gelling agents were used, in most cases containing one or more further constituents. Hydrocolloid concentrations were up to about 5% (except in the case of gelatin which can be used in concentrations of up to about 20 per cent). At a temperature above the gel's setting point air (or inert gases such as nitrogen and carbon dioxide) were incorporated by bubbling an air sparger. The hydrocolloid mixture contained 0-20% of a plasticizer such as glycerol. The resultant gel had 6000-8000 air bubbles per cubic centimeter. Before setting other ingredients such as up to 20%, sugar substitutes (up to 1%), salts up to about 1%), colors at their respectively accepted levels, taste enhancers up to 1000 ppm and flavoring were added. The air filled gels were frozen by several techniques, including regular freezing blast freezing and nitrogen freezing etc., and dried by techniques such as freeze dehydration, drying in a vacuum, or even regular drying when a low volume product was desired.

Gas-filled gels were alternatively produced by putting the above-mentioned food gels in a sealed chamber with liquid containing the same ingredients. Carbon dioxide, nitrogen and the like were then compressed into a chamber. The chamber was later opened abruptly causing the inclusion of air bubbles in the gel. Gas filled gels were dried as described above.

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Another system, was designed to use nitrogen from a biological source. Yeasts were incorporated into gels containing the above mentioned ingredients. Gels were placed in sucrose, glucose, fructose or other sugar solutions. Sugar  
5 diffused into the gels, and carbon dioxide bubbles were formed and trapped within the gel matrix. Gas bubbles content was a function of yeast and sugar contents, temperature of diffusion, gel dimension, etc. Different gel textures were achieved by changing the percentage of yeast,  
10 10 to 10 cells per gram, changing sugar type and content (0.2-30%) or changing temperature.

Gas filled gels were also produced by incorporating calcium carbonate (up to about 3%) and putting the gels in an acid solution (up to about 2.5%). After a short period of  
15 diffusion, gas was produced and trapped within the gel matrix. After freezing and drying as described above, sponge-like materials were obtained. Different gels were manufactured by changing the production order. First, regular gels (including plasticizer and other ingredients)  
20 were produced. Later acid was incorporated by diffusion and gels were put inside a calcium salt source. Carbonates diffusing into the gel were decomposed by the acid, producing a gas-filled gel.

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A special gel, suitable for sponge production was produced by incorporating hydrocolloids inside the gel matrix. Agar, agarose, starch, pectin, alginate and the others at concentrations of up to about 3% can be supplemented to the  
5 above mentioned ingredients. Enzymes, such as an industrial blend of pectolytic materials were diffused into the gel to cut the hydrocolloid and to enable polymer fragments to diffuse out to the solution. Upon drying a sponge-like material had been produced. When agarose is incorporated  
10 into the initial gel, heating a water solution at 450C and the addition of sodium iodide is necessary to decompose and diffuse out the agarose.

An emulsion composed of different percentages of oil in water (0-70%) was gelled using one or more of the above  
15 mentioned hydrocolloids. After gelation a slow heating process was applied, transforming the gel into a porous structure which produced sponge upon drying.

In the following parts are by weight.

Example 1:

20 An air-filled gel was prepared as follows:

Sodium alginate	2
Calcium hydrogen orthophosphate	1
Calcium carbonate	1
Glucono delta-lactone	1
25 Citric acid	2

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Alginate powder 1% w/w, calcium hydrogen orthophosphate (CaHP04) 1% and 1% calcium carbonate were added slowly to stirred cold distilled water (100C) until complete dissolution of the ingredients. A freshly prepared solution of 1% glucono-delta-lactone was then admixed with this solution using vigorous stirring. The alginate solution was poured into a plastic container (10X10X8 cm) and let to set there. After 48 hours specimens were taken from the slab using a cork borer and immersed in citric acid solution 2%. The volume of the citric acid solution was about 100 times the volume of a single gel specimen to guarantee excess acid.

With the diffusion of the citric acid solution there were formed carbon dioxide bubbles, part of which were entrapped in the gel. There resulted a gel containing about 6,500 bubbles per cubic centimeter and the gel was transferred to cold storage at -20 degrees C and afterwards to drying while frozen, at -50 degrees C and at 40 mm pressure. There was obtained an edible sponge, devoid of any caloric value.

It is possible to introduce into the acid solution a small concentration of a sweetening agent, such as 0.5% or less saccharin or food color (10 ppm tetrazine) so as to obtain as final product a sweet tasting yellow colored calory-less edible sponge.



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Example 2

A sponge was prepared as in Example 1, but which has nutritional value. The citric acid solution used contained 12 per cent sucrose and 25 ppm red color (Ponceau 4). After 5 about 3 hours the gel was frozen in a blast freezer during about 2 hours, and lyophilized at -45 degrees C at 30 mm pressure.

There was obtained a sponge having a density of about 0.07 g/ml and a caloric value of about 0.5 cal/gram.

10 Example 3

Agar	1
Pectin	1
Water	98

The agar was dispersed in water and after 10 minutes 15 stirring, the solution was heated to 95 degrees C for 2 minutes and cooled down to 70 degrees C. At this stage the pectin was slowly introduced into the solution, and after cooling there was obtained an agar-pectin gel. This was cut up into desired size and introduced into a 1,000 ppm solution of pectolytic enzymes (commercially available). 20

This constitutes a large excess of such enzymes respective the gel. The system was warmed to 38 degrees C and maintained at this temperature during 5 hours. The excess of

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the enzyme was removed by immersion in water at 38 degrees C during half an hour, and this was repeated 3 times. The gel was frozen in liquid nitrogen and freeze dried. There was obtained a product of a density of from about 0.03 to 5 about 0.1 g/ml.

Example 4

	Carrageenan	1.5
	Konjak mannan	1.5
	Potassium chloride	20
10	Soya oil	20
	Water	76

The konjak mannan (a type of hydrocolloid) was dispersed and dissolved in the water which contained 1% potassium chloride. After warming to 70 degrees C, kappa- carrageenan was added 15 and the solution was stirred until this dissolved. After cooling to 45 degrees C, and in any case to above the setting point of the carrigeen. Then soya oil was added with vigorous stirring to homogenization and the resulting suspension was cooled rapidly to room temperature. This 20 prevents separation of the oil. The gel, containing the oil, was left under refrigeration for 24 hours and introduced into water at 35 degrees C under vigorous stirring. Thus part of the oil is separated, and the remaining gel was frozen and freeze dried. There was obtained a spongy edible 25 product, density: 0.075 g/ml, edible value: about 0.8 cal/g.

Example 5

There was prepared a 2% solution of gellan, and 0.2% calcium chloride (or 2% agar without such additive) or 2% carrageenan with 1% of potassium chloride, or of 1% xanthane and 1% locust bean). The gellan solution was prepared by gradually adding gellan powder to an aqueous solution of the calcium chloride at about 90 degrees. The solution of gellan was cooled to about 40 degrees centigrade or less, so as to bring about gellification. At this stage there was added to one liter of the solution a suspension of 10 of baking yeast of the saccharomyces type, and the solution is cooled rapidly to obtain gellification. In order to avoid a drastic reduction of the active yeast cells one has to work with a hydrocolloid which sets at room temperature. The thus obtained gels were cut into circular disks of about 20mm diameter and 20mm height, and inserted into a 10% sucrose solution. The sucrose diffuses into the gel and the yeast ferments the sugar resulting in carbon dioxide bubbles which are entrapped in the gel (about 10,000 bubbles per cubic centimeter). The gel containing the carbon dioxide, which contains also residual sugar and ethanol produced during the fermentation, is frozen and dried, resulting in an edible sponge of unique structure.

It is possible to carry out such processes with beads of the gel and thus obtain spongy products for use in biotechnology.

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Example 6:

A run was carried out with a solution of 2% into which there was introduced a gas such as oxygen, carbon dioxide, nitrogen or air, and after gellation, cutting up to desired shapes, these are subjected to freeze drying, as in preceding Examples.

Example 7:

Gels produced according to Example 5 or 6 can be inserted into a pressure vessel, and after equilibration, the pressure is suddenly released, resulting in incorporation of air bubbles. After freezing and drying a sponge is obtained.

## CLAIMS:

1. A sponge of predetermined characteristics of water absorption, biodegradability and pore size and structure, being the product of expansion of a suitable hydrocolloid.
2. A sponge according to claim 1, where the sponge is  
5 formed by foaming one or more hydrocolloid selected from agar, carrageenan, gelatin, alginate, starch, pectin, gellan, kunjak mannan, xanthan locust bean.
3. A sponge according to claims 1 or 2, of edible components.
4. A sponge according to claim 3, containing a predeter-  
10 mined quantity of a high-calory content ingredient.
5. A sponge according to any of claims 1 to 4, containing a plasticizer.
6. A sponge according to claim 5, containing glycerol, sorbital or another suitable polyol as edible plasticizer.
- 15 7. A sponge according to any of claims 4 to 6, where the sponge contains a sugar or sugar substitute, possibly with a flavoring agent or taste enhancer.
8. A sponge according to any of claims 1 to 7, containing bubbles of a gas other than air.
- 20 9. A sponge according to any of claims 1 to 8, having a specific density from about 0.01 g/cm to about 0.4 g/cm.

10. A process for producing a sponge as claimed in any of claims 1 to 9, which comprises preparing a solution of one or more hydrocolloid, as herein defined converting to a gel form, possibly with one or more additional ingredients, and  
5 introducing the required quantity of gaseous medium by bubbling a sparger.

11. A process for the production of foams according to any of claims 1 to 9, where a gel of the constituents is formed, this is sealed in a chamber with a liquid containing the same  
10 ingredients, introducing a gas into the chamber at a high pressure and abruptly releasing such pressure, followed by freeze drying the material to obtain the sponge.

12. A process for the production of a sponge as claimed in any of claims 1 to 9, where a gel is formed of the required  
15 ingredients introducing fermenting microorganisms into said gel, contacting this with a nutrient solution containing the required nutrients for the microorganism so that the carbon dioxide resulting from the fermentation results in the formation of a sponge, which is subsequently processed to  
20 obtain the final product.

13. A process for the production of a sponge as claimed  
in any of claims 1 to 9, where a carbonate is included  
in the gel, and this gel is contacted with an acid  
solution, or an acid is incorporated into the gel and  
5 contacted with a carbonate solution resulting in carbon  
dioxide formation, which results in the formation of a  
sponge.

# INTERNATIONAL SEARCH REPORT

Int. Application No

PCT/EP 94/00107

## A. CLASSIFICATION OF SUBJECT MATTER

IPC 5 C08L5/00 A23L1/05 C08J9/00

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 5 C08J A23L C08L C08B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US,A,3 334 052 (F. W. A. KURZ) 1 August 1967 see column 1, line 60 - column 2, line 7 see column 2, line 68 - column 3, line 2 ---	1,2,8-10
X	CA,A,961 340 (GENERAL FOODS CORPORATION) 21 January 1975 see example I --- -/--	1-4,11

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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# INTERNATIONAL SEARCH REPORT

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## C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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Information on patent family members

International Application No

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